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TEMPLATE SYNTHESIS OF METAL MICROTUBULE ENSEMBLES UTILIZING
CHEMICAL, ELECTROCHEMICAL, AND VACUUM DEPOSITION TECHNIQUES

Charles J. Brumlik, Vinod P. Menon, and Charles R. Martin^{*}
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

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To whom correspondence should be addressed.

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ABSTRACT

Microtubules are an interesting type of microstructure that resemble miniature drinking straws. Such tubular microstructures are found in nature. In addition, we and others have been investigating strategies for making synthetic analogs. We are especially interested in the idea of making metal microtubules. Four procedures for preparing metal microtubules are described in this paper. The general approach, called template-synthesis, entails using the pores in a microporous membrane as templates for forming the tubules. Microporous anodic aluminum oxide membranes and nuclear track-etch membranes are used as the template membranes. Gold and silver microtubules are made with outer diameters as small as 200 nm. These microstructures are characterized by scanning electron microscopy.

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**Template Synthesis of Metal Microtubule Ensembles Utilizing Chemical, Electrochemical
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by

C. J. Brumlik, V. P. Menon and C. R. Martin

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Colorado State University
Ft. Collins, CO 80523**

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INTRODUCTION

Organic microtubules are chemical or biological microstructures that resemble miniature soda straws (1-25). Tubular structures of this type occur in nature, for example, biological microtubules composed of the protein tubulin (26-28) and "buckytubes" composed of carbon (9,29-31). Interest in synthetic analogs of these tubular microstructures was sparked by Schnur et al. who discovered a family of lecithins that self-assembled into organic microtubules (6-8,24,25,32-38). A number of technological applications have been suggested for these microtubules (11,24). We have recently developed a new way to make such organic microtubules (3-5). This method entails the use of a microporous membrane as a template. The microtubules form on the pore walls in the membrane. As a result the outer diameter of the tubule formed is determined by the diameter of the pores in the membrane. We call this concept "template synthesis" because the pores in the membrane act as templates for the formation of the tubules. We have used two types of microporous membranes to synthesize tubules of this type; both contain well-defined pores with sub-micron diameters. The first membrane type is a porous anodic aluminum oxide (39) and the second is a nuclear track-etch filter membrane (40-42).

More recently, we and others, have become interested in the synthesis of *metal* microtubules (2,6,21,38,43,44). Such tubules are of interest because they can have good electrical conductivity, magnetic susceptibility, and low electron work functions. Furthermore, metal microtubules can be used as porous electrodes for flow electrolysis (45), substrates for surface enhanced raman spectroscopy (SERS) (21,46),

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ensembles of microring electrodes (47), field emission electrodes (20,21), quantum devices (48), memory devices (49), and electroplated electronic circuit board through-holes (50). We have recently described a variant of our template method that allows for the synthesis of metal microtubules (2). This method entails electrochemical deposition of gold into the pores of a chemically-modified alumina membrane (2). We have since expanded on, and modified, this electrochemical method. We have also explored alternate methods for forming metal microtubules. The results of these investigations are described here.

EXPERIMENTAL

Membranes. Two types of microporous membranes were used in these studies. The first was a porous aluminum oxide made by electrochemical anodization of aluminum. Membranes of this type can be made with pore diameters ranging between 10 nm and 300 nm (51,52). Such membranes are available commercially as a filtration membrane with pores that are 200 nm in diameter (Anopore™ (39)). These membranes have a porosity of 40 to 65% (5×10^8 to 1.6×10^9 pores/cm²) (39,53,54). This commercially available membrane was used for these studies. A scanning electron micrograph of the surface and edge of such a membrane is shown in Figure 1A. The pores are oriented perpendicular to the surface and are approximately hexagonal packed. The pores also have a very small pore size distribution (55).

The second type of membrane used was made by nuclear track-etch technology (21,56). Heavy particles (such as uranium fission fragments) create single-event "damage tracks" in insulators (21,56,57). These tracks can be chemically

etched at a greatly enhanced rate (compared to the bulk material). Irradiation of a membrane with a beam of heavy particles followed by chemical etching results in a membrane with randomly distributed pores (21,40-42,58). The pores can have diameters anywhere between 10 nm and tens of microns. Pore-size distributions are very small (56). These membranes are also often called nuclear track filters (59), or screen membranes (41). This technology has been used to prepare track-etched polymer (e.g. polycarbonate (60,61)) and mica microfilters (62-65). Commercial membranes are made by Nuclepore (40), Poretics (41), and Cyclopore (42). Figure 1B shows an electron micrograph of the surface and edge of a Nuclepore membrane with 2 μ m diameter pores. The membrane shown in this figure was freeze fractured in liquid helium. The edge of the membrane appears ragged because it is difficult to break the membrane cleanly. Membranes of this type with pore diameters of 400 nm were used for these studies.

Materials and Reagents. Gold (99.99%, Credit Suisse), 2-cyanoethyltriethoxysilane (Petrarch/Hüls), anhydrous hexadecane (99+%, Aldrich), tin(II) chloride anhydrous (98%, Aldrich), silver nitrate (99.9%, Spectrum), ammonium hydroxide aqueous solution (30%, Mallinckrodt), potassium sodium tartrate (AR, Mallinckrodt), magnesium sulfate (99.9%, Fisher), hydrochloric acid (SP, Mallinckrodt), silver chloride (Sigma, crystalline pfs), sodium carbonate anhydrous (Sigma, ACS Reagent), potassium ferrocyanide (Aldrich, ACS reagent), and potassium thiocyanate (Sigma, ACS Reagent) were used without further purification. 18 M Ω water was used to make all

aqueous solutions. This water was made by passing house distilled water through a four-cartridge Millipore water purification system.

The gold electroplating solution was Orotemp 24 neutral gold cyanide (5 dwt./L, Technic). This solution was diluted to 2 to 4 dwt./L for the flow electrolysis experiments. Silver was electroplated from a homemade silver thiocyanate bath containing 1.43 g AgNO_3 , 2.0 g Na_2CO_3 , 3.0 g $\text{K}_4(\text{Fe}(\text{CN})_6)$, and 15 g KCNS in 200 mL water (66). The silver electroplating solution was stored in the dark and filtered periodically. Counter electrodes included a 50 X 50 X 1 mm silver sheet (99.9%, Aldrich) for silver electroplating and a large area platinized niobium mesh (Technic) for gold electroplating. Stirring was accomplished with a magnetic stir bar. All current densities were calculated relative to the fractional pore area of the membrane; i.e. the fraction of the membrane surface that is pore area. The fractional pore area for the Anopore membrane is 0.65. The fractional pore area for the Nuclepore membrane is 0.126.

Electroless silver was deposited using a two-part (A and B) bath (67). Part A consisted of 454 g silver nitrate, 355 mL ammonium hydroxide, and 4.54 L water. Part B consisted of 1,590 g Rochelle salt (potassium sodium tartrate), 114 g Epsom salt (magnesium sulfate), and 3.64 L water. Equal volumes of A and B were mixed with 14.1 parts water. The working temperature of the electroless silver electroplating bath was 35 °C. The activator solution was comprised of 2 g/L anhydrous tin (II) chloride and 2 mL/L concentrated hydrochloric acid.

Instrumentation. A peristaltic pump with a variable-speed drive (Cole-Parmer MasterFlex L/S) and 6.4 mm I.D. tubing (C-Flex #17, Cole-Parmer) was used in the flow experiment. Electrochemical experiments were conducted with a PARC 173 potentiostat and 179 coulometer. Scanning electron micrographs were obtained with a Philips 505 scanning electron microscope with a LaB₆ source.

Thin film deposition equipment included a thermal evaporator (DV502A, Denton Vacuum) with a 2 kV-A power supply and an argon plasma sputter coater (Hummer I, Technics). The following precautions were taken to prevent heat damage to the polycarbonate template membranes during metal evaporation: 1) A tantalum heat shield with a 1.75" X 0.75" opening was placed 0.5" above the evaporation boat (S38A-AO-W, R.D. Mathis); 2) The membrane was positioned at least 5" above the boat; 3) The electrical feedthroughs were water cooled; 4) The evaporation boat was heated only until a metallic gold film was seen on the membrane; and 5) two 1.25" long pieces of twisted tungsten wire (4 X 0.03", R.D. Mathis) were used in the evaporation boat to provide a surface for evaporation of the gold. This decreased the extent of sputtering (kroiling) of the molten metal. Kroiling can cause small drops of molten metal to hit the membrane along with the desired metal vapor.

Microtubule fabrication methods. In this paper, we demonstrate four methods of making metal microtubules using microporous template membranes. Experimental details of each method are presented below.

Evaporation/Electroplating. Spohr et. al. have made large diameter (e.g. 3 μ m) metal microtubules by evaporating a metal, at normal incidence, onto a nuclear track-

etch filter (20,21). The metal vapor migrated a short distance into the pores (68,69) and then adhered to the pore walls. Free standing tubules were obtained by dissolving the host microporous membrane. However, this method can only be used to form tubules with outer diameters in the micron range. When metal is deposited into membranes with smaller pores, solid metal fibers are obtained.

We have improved upon Spohr's evaporation method (20,21) by combining vacuum deposition with an electroplating method. A schematic of this vacuum/electroplating hybrid method is shown in Figure 2. A very thin (ca. 20 nm) gold film is first vacuum evaporated on the surface of a Nuclepore polycarbonate filter (pore diameter = 400 nm). This film is too thin to cover over the pores at the membrane surface. As a result, metal also deposits part way down the pores to yield extremely thin-walled gold tubules (Figure 2, Part A). These tubules can be strengthened by using them as cathodes to electrochemically deposit a metal onto the tubule wall (Figure 2, Part B). The resulting thickened tubules have improved mechanical strength. As a result, the membrane can be dissolved away to expose an ensemble of free-standing tubules (Figure 2, Part C).

Silver (deposited from the homemade silver thiocyanate bath) was used to thicken the tubule walls. Silver was deposited galvanostatically at a current density of $1 \text{ mA}\cdot\text{cm}^{-2}$. The gold-coated membrane was placed in the electrochemical cell with the gold-coated surface facing the silver counter electrode. A custom-made holder was used to mount the gold-coated Nuclepore membrane in the electrochemical cell. This membrane holder is shown schematically in Figure 3. This holder was made of

two 1/8" X 2.6" X 3.6" teflon (PTFE) sheets held together with 1/4" I.D. ultrahigh molecular weight polyethylene channel extrusions (UHMWPE Ultra-Wear® 42-113, Cadillac Plastic). Two 2.6" X 3.6" wax sheets (Parafilm "M", American National Can) were used between the teflon sheets to seal the holder and prevent solution leakage around the microporous membrane. A 1.5" diameter through-hole was cut through one teflon and one wax sheet. The holes were overlapped in order to expose only one side of the microporous membrane to solution. The microporous membrane (1.85" diameter) was sandwiched between the wax sheets. Electrical contact to the gold-coated microporous membrane was made with a strip of gold-coated (thermally evaporated) aluminum foil.

After silver plating, the template membrane was dissolved in dichloromethane. This exposes an ensemble of parallel microtubules connected at their base by a silver-coated gold thin film (Figure 2, Part C). It is also possible to collect the isolated tubules. This is accomplished by dissolving the Ag base layer prior to dissolution of the membrane. The Ag base layer is dissolved by applying a few drops of nitric acid to the membrane surface before dissolution of the membrane. If the membrane is then dissolved the individual silver tubules can be collected by filtration.

Electrodeposition in Pore-Wall-Modified Anopore Membranes. We briefly described this approach for forming microtubules in a recent correspondence (2). This method entails electrodeposition of metal into the pores of a gold-coated Anopore alumina membrane. However, prior to electrodeposition, the pore walls are modified with a silane derivative that interacts strongly with the metal being deposited. For

example, we have used 2-cyanoethyltriethoxysilane as a pore-wall modifying agent for the formation of gold microtubules (2). When gold is electrochemically deposited in the pores, the strong affinity of the organonitrile for gold (70) caused preferential deposition of gold on the pore walls. As a result gold tubules are obtained. Functionalization of the alumina pore walls is easy because silanes react with, and bond strongly to, alumina (2,46,53,71).

This procedure for synthesis of metal microtubules is summarized schematically in Figure 4. The Anopore membrane was first silanized by sonication for 30 seconds in a 0.1 v/v% solution of 2-cyanoethyltriethoxysilane (in anhydrous hexadecane). The silane-treated membrane (Figure 4, Part A) was then heated overnight at 100 °C. A ca. 20 nm-thick gold film was then sputter-deposited from an argon plasma onto one face of the Anopore membrane (Figure 4, Part B).

This gold film was then used as a cathode to electroplate gold down the pore wall. Gold also plates on the surface of the membrane and ultimately covers the surface of the membrane (Figure 4, Part C). The length of the tubules obtained can be varied by varying the amount of gold deposited. We deposited between 0.5 and 4 coulombs per cm² at a current density of 0.5 to 2 mA/cm². Ultimately, the tubules become solid fibers. We have found, however, that tubules with lengths of up to 2 microns can be obtained via this method. Electroplating was accomplished using the membrane holder shown in Figure 3. Finally, the alumina membrane was dissolved in hydrofluoric acid to expose the ensemble of gold microtubules (Figure 4, Part D). This, again, yields an ensemble of parallel gold microtubules connected at their base

to a gold film. Again, the gold film can be dissolved prior to dissolution of the template membrane by applying a few drops of aqua regia. Subsequent dissolution of the membrane frees the tubules. The tubules can then be collected by filtration.

Flow-Assisted Electroplating. The microtubules made by the evaporation/electroplating procedure or by electroplating in pore-wall-modified membranes were limited in use by the eventual closure of one end of the tubules. To increase tubule length of completely hollow tubules, flow electrolysis was used (72,73). The Anopore alumina filtration membranes were used as the synthesis template. In analogy to the electroplating method discussed previously, a ca. 20 nm gold film was first sputtered onto one face of the Anopore membrane. Again, this gold film is too thin to block the pores at the membrane source, but serves to convert the membrane surface into an electrode.

This gold-coated membrane was used as the cathode in the flow-assisted electroplating apparatus shown in Figure 5. This apparatus uses a peristaltic pump to force plating solution to flow through the membrane during the gold plating process. The membrane was held in a 25 mm, threaded filter holder (Nalgene™ in-line filter holder). One end of this holder was ground down so that the membrane was exposed. This end of the holder was then immersed into a beaker of plating solution (Figure 5). The other side of the holder was connected with flexible tubing to a pressure gauge and then to the pump (Figure 5). Gold electroplating solution was passed through the membrane at flow rates of 5 to 100 mL/min. The upstream pressure was monitored via a pressure gauge (0 to 20 psi). A large area platinized

niobium mesh was used as a counter electrode in the beaker (parallel to the membrane). As in the previously described methods, electrical contact to the membrane was made with a strip of gold-coated aluminum foil.

The gold-coated side of the Anopore membrane was placed downstream so that the growing end of the tubules would be exposed to fresh electroplating solution. Electroplating was continued until the pressure started to rise. A large rise in pressure indicated that the tubules were becoming solid fibers due to increasing wall thickness. The Anopore membrane could later be dissolve in hydrofluoric acid as shown in the previously described methods.

Electroless (i.e., Chemical) Metal Deposition. We have used an electroless method to prepare silver microtubules that span the entire thickness of the template membrane. Electroless silver was deposited by the Rochelle salt method (74). This method is summarized schematically in Figure 6. The Nuclepore polycarbonate filters were used as the template membranes. These membranes have a smooth face and a rough face (75). A strip of Scotch-brand tape was attached to the smooth face (Figure 6, Part A). The membrane/tape composite was then activated by sonication in a tin (II) chloride solution (0.2% in 0.02 M HCl) for three minutes or until thoroughly wetted (Figure 6, Part B). The membrane/tape composite was then rinsed several times in 18 M Ω water to remove excess Sn²⁺ and dried. The tape was removed by soaking the composite in diethyl ether (Figure 6, Part C). (The tape prevented Sn²⁺ activation of one side of the membrane and therefore subsequent formation of a silver surface layer (see below) on this side of the membrane.)

The Sn^{2+} activated membrane was then placed in freshly-prepared electroless silver plating solution. The membrane was left in the electroplating solution for ca. 30 minutes. This caused silver to deposit on the activated surface and the pore walls (Figure 6, Part D). The membrane was then rinsed in water and allowed to dry. As in the previous methods, this procedure yields an ensemble of metal microtubules connected to a thin silver base layer. If desired, the membrane can be dissolved at this point to expose this ensemble of tubules. Alternatively, the silver surface layer can be removed (with 25% nitric acid). The membrane can then be dissolved and the tubules connected by filtration.

RESULTS AND DISCUSSION

Four approaches for template synthesis of metal microtubules have been presented. These methods are discussed in the following sections.

Evaporation/Electroplating Method. Figure 7 shows a scanning electron micrograph of an ensemble of 400 nm-diameter silver/gold microtubules made by evaporation of gold followed by electroplating of silver. The host polycarbonate membrane was dissolved in dichloromethane (3-5,76,77). Dissolving away the host membrane affords an opportunity for observing the metal microtubules. Clearly, metal is deposited along the host membrane's pore walls. Furthermore, the exposed metal microtubules retain the size and circular shape of the pores in the host membrane. There are also no apparent macroscopic defects in the metal microtubules.

The smallest diameter tubules, that we made via this method, had outer diameters of 400 nm. The maximum tubule length that could be achieved for this

diameter was ca. 1 μm . This tubule length is only slightly greater than the depth within the pores that metal is evaporated (68,69). Therefore, as indicated in the Experimental section, electroplating acts only to thicken the walls of these tubules. This wall thickening gave the tubules structural strength so that they could be self-supporting without the aid of the host membrane.

Pore-Wall-Modification Method. An electron micrograph of an ensemble of 200 nm O.D. gold microtubules prepared via this method is shown in Figure 8. This free standing ensemble of tubules was obtained by leaving the gold base film (Figure 4) intact and dissolving the alumina membrane in hydrofluoric acid. The length of the tubules obtained via this method depends on the amount of gold that is deposited. Very short tubules are hollow throughout. Figure 9 shows a scanning electron micrograph of a side view of such short, completely-hollow, tubules. (These tubules are not perfectly cylindrical because the pores in the Anopore host membrane are often tapered at their ends.) This method can be used to grow hollow tubules that are as long as 3 μm . We have proven that tubules of this length are hollow because, after dissolution of the base gold layer, liquid flows through the tubule-impregnated membrane. However, attempts to prepare larger tubules via this method yielded solid gold fibers rather than hollow gold tubules.

An obvious question arises - is the silane layer (Figure 4, Part B) really necessary to obtain tubules in these membranes? The answer to this question is yes. If gold is plated under identical conditions in a non-silanized (i.e. as-received) Anopore

membrane, only solid gold fibers are obtained (53,54). This preferential pore wall deposition is caused by the strong interaction between the organonitrile and gold (70).

Flow-Assisted Electroplating Method. An ensemble of gold microtubules prepared by this method is shown in Figure 10. These tubules have an O.D. of 200 nm. We have prepared tubules as long as 3 μm via this method. That these tubules are hollow is proven by the fact that electrolyte flowed through the tubule-impregnated membrane during the electroplating process. Attempts to make larger tubules caused a dramatic rise in pressure in the flow cell indicating that the tubules were closing-off to form solid fibers.

Electroless Deposition Method. A scanning electron micrograph of a collection of 400 nm-diameter silver microtubules prepared via this method is shown in Figure 11. This method for forming microtubules is by far the most convenient, versatile and powerful. First, this method requires no instrumentation or electrochemical cells. Second, metal deposition proceeds from the pore wall itself rather than from a base layer of metal (as in the electrochemical deposition methods). As a result, there is no competition between elongating the tubule and closure of the tubule to form a solid fiber. This competition limits the lengths of the tubules obtained via the various electrochemical methods (see above) to ca. 3 μm . Furthermore, metal deposition proceeds uniformly down the entire length of the pore. As a result, tubules that span the entire thickness of the membrane are obtained. For example, because the membrane used to prepare the tubules in Figure 11 was 10 μm thick, tubules of this length are obtained. This is significantly longer than the tubules obtained by the other methods. Furthermore,

even longer tubules could be prepared in thicker membranes. For example, Cyclopore Inc. (Belgium) sells polycarbonate membranes of this type that are 50 μm in thickness.

It is also important to point out that tubules with monodisperse lengths are obtained via this method because the membranes have uniform thicknesses. In addition, tubules composed of a variety of metals can in principle be prepared. To date, we have prepared silver and gold tubules of this type. Finally, tubules with extremely small diameters can be prepared. We have used this method to prepare tubules with diameters as small as 30 nm. We have proven that tubules of this, extremely small, diameter are hollow because liquid flows freely through the tubule-impregnated polycarbonate membrane. Membranes of this type are commercially available with pores as small as 15 nm.

CONCLUSION

We have described four methods for preparing metallic microtubules. Of these, the electroless method is the most versatile. This method could prove useful if any of the proposed technological applications (10,11,16,18,22,43,46,78,79) of such tubules are brought to fruition.

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REGISTRY NO.

Aluminum oxide [1344-28-1]

2-Cyanoethyltriethoxysilane [17932-62-6]

Nuclepore [12673-61-9]

Gold [7440-57-5]

Silver [7440-22-4]

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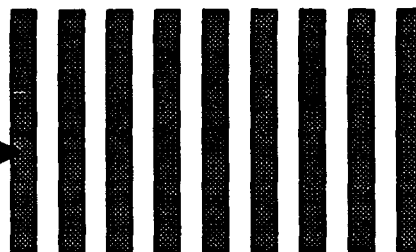
FIGURE CAPTIONS

- Figure 1A** Electron micrograph of a 200 nm pore-diameter anodic aluminum oxide Anopore membrane.
- Figure 1B** Electron micrograph of a nuclear track-etch Nuclepore membrane, with 2 μm diameter pores. The membrane was freeze fractured in liquid helium.
- Figure 2** Schematic of the evaporation/electroplating procedure for forming metal microtubules.
- Figure 3** Schematic of the membrane holder used for electroplating.
- Figure 4** Schematic of the procedure used to prepare metal microtubules by the pore-wall-modification method.
- Figure 5** Schematic of the flow-assisted electroplating cell used to make metal microtubules.
- Figure 6** Schematic of the electroless deposition procedure for forming metal microtubules.
- Figure 7** Electron micrograph of a microtubule ensemble with 400 nm O.D. gold/silver composite microtubules. Tubules were made using the evaporation/electroplating procedure. The template membrane (a Nuclepore polycarbonate filter) was dissolved in methylene chloride.
- Figure 8** Electron micrograph of a microtubule ensemble containing 200 nm O.D. gold microtubules. Tubules were prepared using the pore-wall-modification method. The template membrane (an Anopore alumina filter) was dissolved in hydrofluoric acid.
- Figure 9** Electron micrograph of the edge of a gold microtubule ensemble with completely hollow short gold microtubules. These tubules were prepared using the pore-wall-modification method.
- Figure 10** Electron micrograph of a microtubule ensemble containing 200 nm O.D. gold microtubules. Tubules were made by the flow electrolysis method. The membrane was dissolved in hydrofluoric acid.
- Figure 11** Electron micrograph of silver microtubules (with the host membrane dissolved away) made by the electroless deposition method.



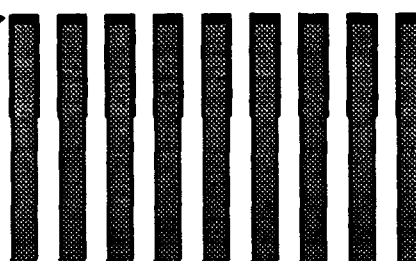


**Microporous
Template
Membrane**

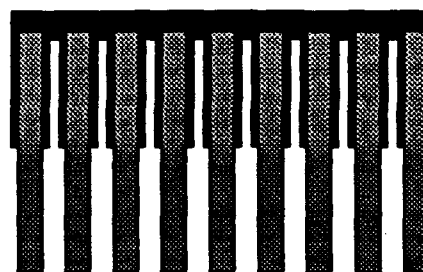


**Vacuum Evaporate
Au on Upper Surface**

Gold Coating



**Electroplate Ag to
Thicken Tubule Wall**

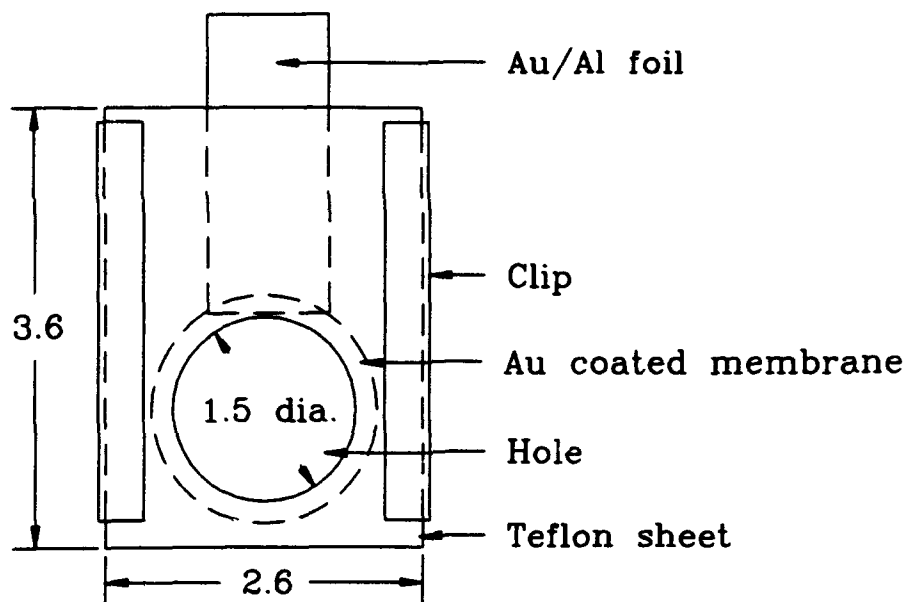


**Dissolve Nuclepore
Template Membrane**

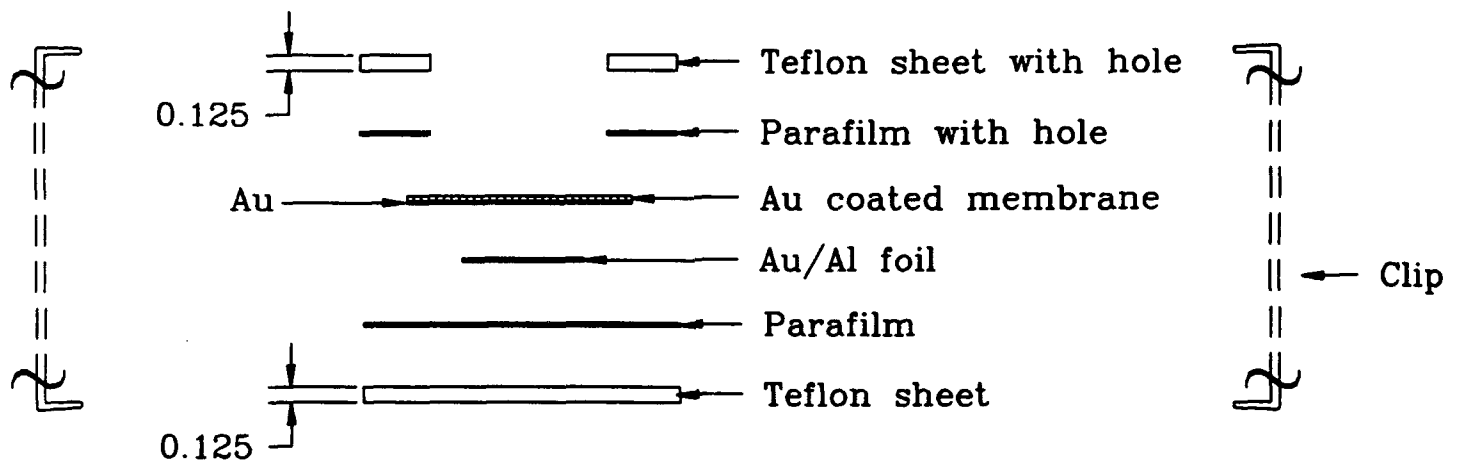
**Ensemble of
Au / Ag
Microtubules**



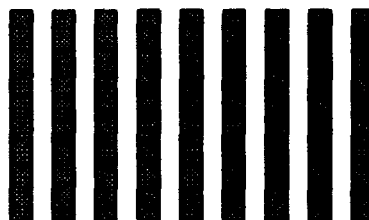
Top View



Exploded Side View

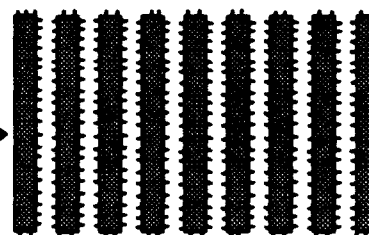


**Microporous
Template
Membrane**



**Membrane Treatment
With Silane**

**Silanized
Membrane**

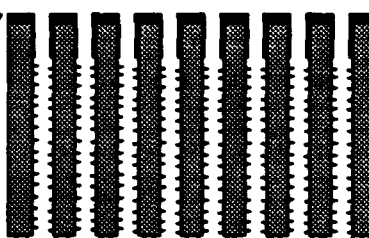


(A)



**Sputter Coating
of Gold Film**

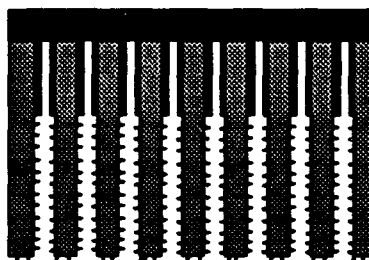
Gold Film



(B)



**Electroplating
of Gold**



(C)

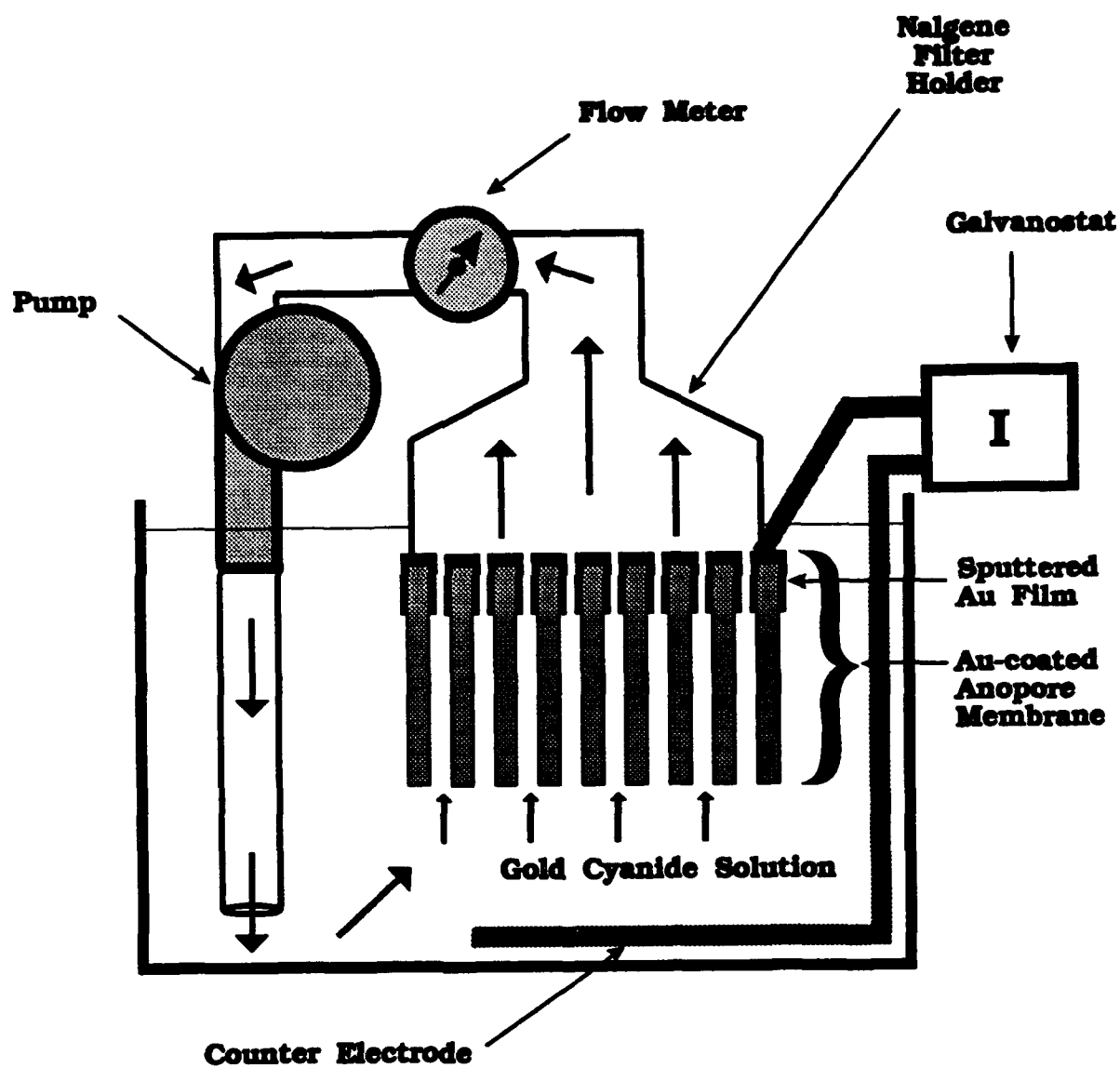


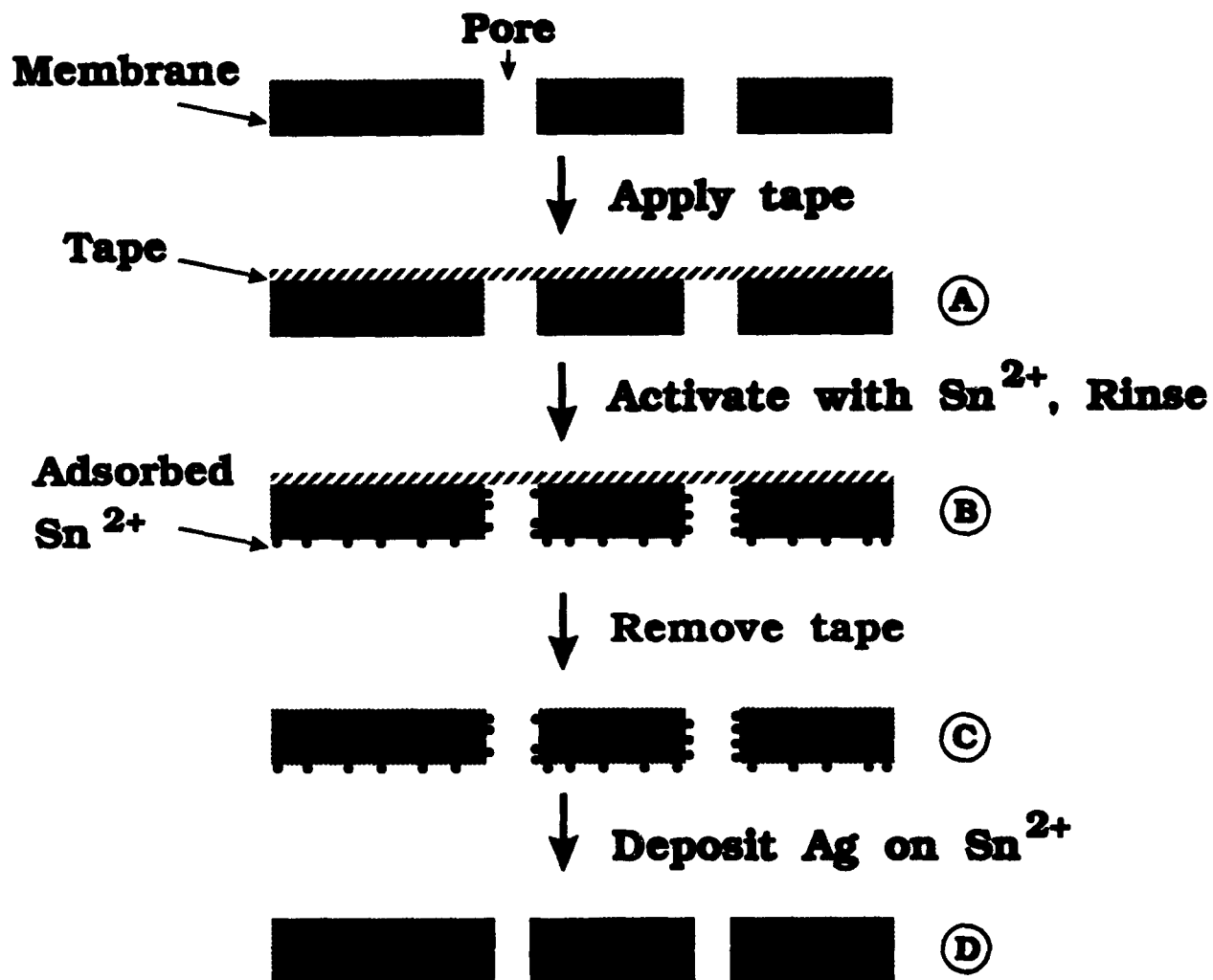
**Dissolution
of Membrane**

Tubules



(D)

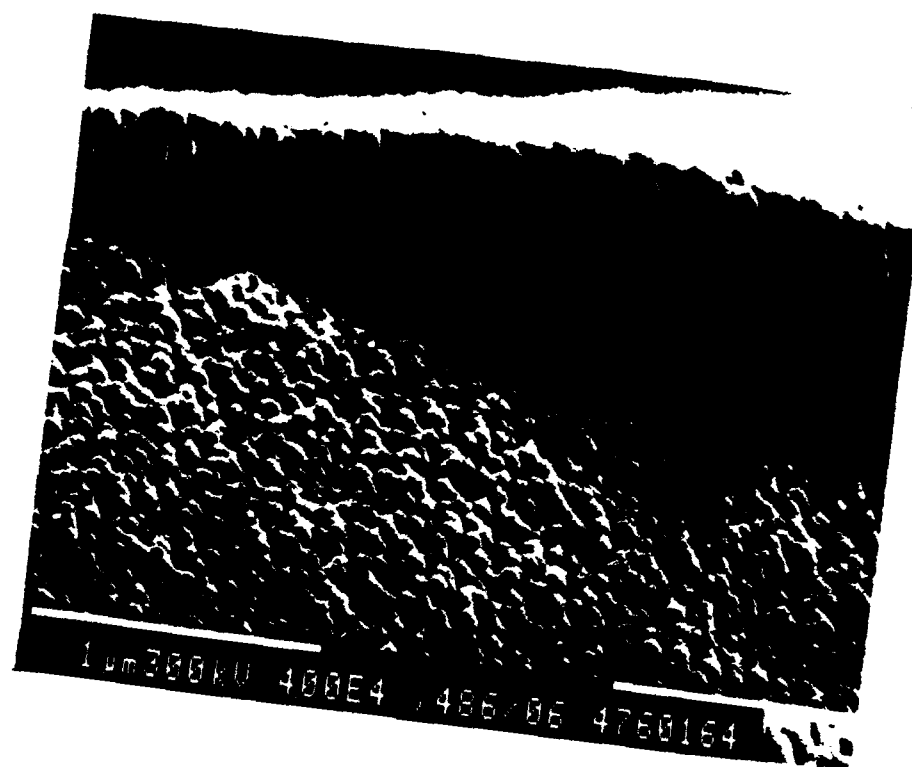




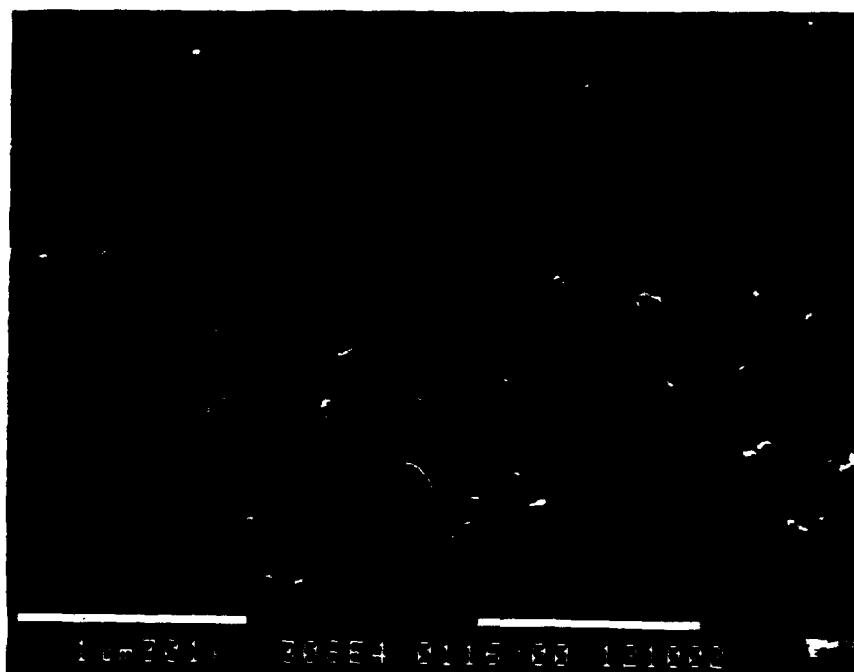


— 1 μm





10m30000 400E4 486/06 4780164 11.5



10-22-10 00:00:00 10-22-10



10 μ m 30.0kV 9.15E3 0071/06 0.4 MAG